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Quantitative Analysis of Residual Monomer in PMMA by Thermal Desorption-GC-MS

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Application Note

Polymer

Abstract

This application note demonstrates quantitative analysis of monomer contamination in a polymer by performing TD-GC-MS.

Introduction

Acrylic polymers are prepared from acrylate monomers and are widely used in cosmetic and medical products. During the polymerization process, certain level of monomer is left unpolymerized. The exact amount of such residual monomer became an interest of quality control since the sensitive applications could be regulated by the FDA[1]. Although these QA analysis are frequently done by solvent extraction, thermal analysis offers some distinct advantages. First, it is a green method without solvent to concentrate or dispose. Secondly, since the analysis does not include a large solvent peak, the technique is a sensitive way to identify traces of compounds which might be masked by solvent injection. Finally, larger sample may be analyzed with better homogeneity, as opposed to an aliquot from a solvent extraction.[2]

While the Pyroprobe's normal function is to use pyrolysis as a tool to identify polymer materials, it actually offers a full suite of thermal analysis tools including Thermal Desorption, Dynamic Headspace, Photochemistry, Evolved Gas Analysis , Tandem Reactor and even SPME based on the nature of the application. Following the Pyroprobe Application Decision Making Tree[3], a piece of polymethyl methacrylate (PMMA) material was analyzed to quantify the residual monomer, which is methyl methacrylate. After an Evolved Gas Analysis screening was performed, a thermal desorber attachment was picked for thermal desorption-GC-MS to calculate the amount of residual monomer in the material.

Experiment Setup

The sample was first added into a DISC (Drop-In-Sample Chamber) tube and then analyzed using Evolved Gas Analysis (EGA) as the first screening step by following the Pyroprobe Application Decision Making Tree.

The thermal desorption attachment used in the later study is an option available to the Pyroprobe 6200, the model with a built-in sorbent trap. This thermal desorption attachment takes 1/4" OD by 3.5" Length inert coated thermal desorption tube, where a large amount of sample could be placed.

EGA

Pyroprobe with DISC	
Initial:	50°C
Final:	1000°C
Ramp Rate:	100°C per min
Interface:	300°C
Transfer Line:	300°C
Valve Oven:	300°C

GC/MS	
Column:	Fused silica (1m x 0.10mm)
Carrier:	Helium 1.25mL/min
Split:	80:1
Injector:	360°C
Oven:	300°C
Ion Source:	230°C

Thermal Desorption

Pyroprobe 6200 with 1/4” Tube Desorber

Tube Desorb Temp:	80°C
Desorb Time:	10min
Purge Gas:	He 20mL/min
Trap Type:	Tenax TA
Trap Rest:	40°C
Trap Final:	300°C
Transfer Line:	300°C
Valve Oven:	300°C

GC-MS

Column:	5% phenyl (30m x 0.25mm)
Carrier:	Helium 1.25mL/min, 20:1 split
Injector:	360°C
Oven:	40°C for 2 minutes 12°C/min to 150°C
Ion Source:	230°C
Mass Range:	35-600amu

Results and Discussion

An initial screening with Evolved Gas Analysis (EGA) shows several small rises in the baseline, starting around 200 °C. The main large peak is positioned at 425 °C. The mass spec data from the small rises all match to methyl methacrylate, Hirata et al. reported that thermal degradation of PMMA occurs in 3 parts: 1- decomposition of weak head-to-head bonds 2- decomposition of unsaturated chain ends, and then finally 3- Unzipping of the polymer chain[4]. This thermal degradation complicates the goal of this application as to quantify the native monomer residue. From the area integration, it is also noticed that the monomer residue, if there is any, has very low concentration comparing to the main polymer.

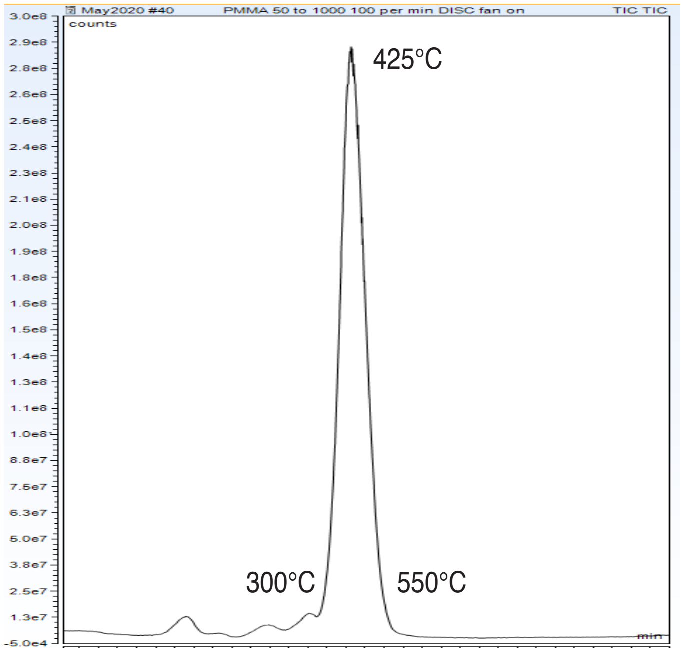

Figure 1. Evolved Gas Analysis of PMMA from 50°C to 1000°C at 100°C per minute

Following the flow path in the Pyroprobe Application Decision Making Tree, a thermal desorber attachment was used to study target analytes at very low concentration, where a larger amount of sample is needed. A thermal desorption temperature of 80°C was chosen to adequately extract residual monomer without decomposing the polymer based on the data shown in the EGA. Figure 2 shows the residual methyl methacrylate monomer (MMA) collected from thermal desorption of PMMA. After the desorption time, the same sample was run again under the same condition. The data is plotted in blue line, which shows a complete thermal extraction from the previous run, as well as demonstrates that no MMA is not being produced by degradation of the PMMA under this condition.

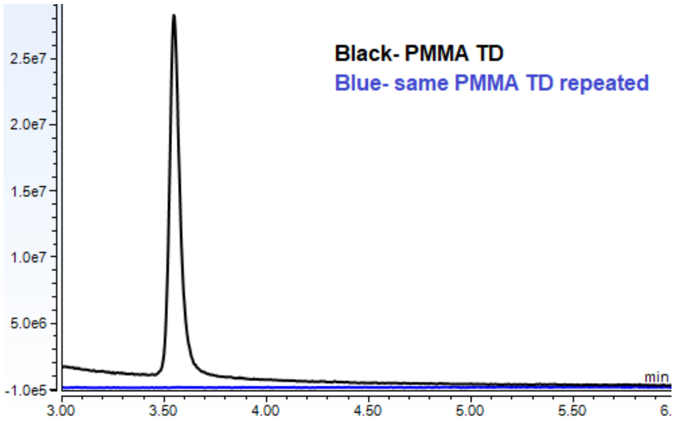

Figure 2: Thermal desorption of PMMA at 80°C for 10 minutes followed by a second Thermal desorption.

To quantify the amount of residual monomer, an MMA standard was diluted in acetone to a final concentration of 500 µg/mL as the stock solution. Four aliquots of this stock solution with volumes at 0.5 µL, 1 µL, 1.5 µL and 2.0 µL for total amounts of 250 ng, 500 ng, 750 ng, and 1000 ng respectively were thermally desorbed using the same method. The calibration is shown in Figure 2. Using this calibration curve, a 30 mg sample was calculated to contain 443 ng of residual MMA, which is 14ppm.

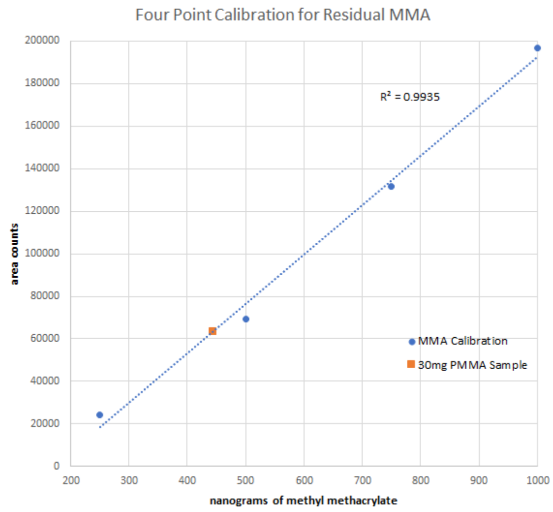

Figure 2. MMA Calibration Curve with the unknown sample added

Conclusions:

A polymethyl methacrylate polymer sample with monomer contamination was analyzed quantitatively by a TD-GC-MS method by a CDS 6200 Pyroprobe, which was demonstrated as a useful instrument in investigating the monomer contamination in a polymer at the ppm level.

References

1 Methacrylate Producers Association, Inc. http://www.mpausa.org/

2 T. P. Wampler, Analysis of Food Volatiles using Headspace-GC Techniques, in R.Marsili (Ed.) Techniques for Analyzing Food Aroma, Marcel Dekker, New York, 1997.

3. Pyroprobe Application Decision Making Tree., CDS Analytical, 2020..

4. Hirata T, Kashiwagi T and Brown JE. Thermal and Oxidative Degradation of Poly(methylmethacrylate):Weight Loss. Macromolecules. 1985;18:1410-1418.